

PATENT SPECIFICATION

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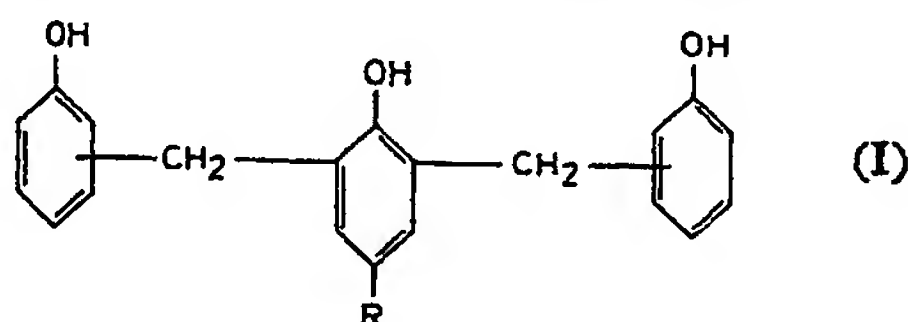
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(54) POLYHYDROXY PHENOLS AND PROCESS FOR THEIR PREPARATION

(71) We, SOCIETA' ITALIANA RESINE S.I.R.S.p.a. an Italian Joint Stock Company of 33 Via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new polyhydroxy phenols defined by the following formula:



where R is an alkyl radical containing from 1 to 10 carbon atoms, the methylene bridge being bonded to the central phenol ring in the ortho-positions in relation to the hydroxyl group, and to the other phenol rings in the ortho- or para-position in relation to the hydroxyl group.

The invention also concerns a method for preparing the said polyhydroxy phenols, by reacting formaldehyde with phenol substituted in the para position with an alkyl group with from 1 to 10 carbon atoms, to give the dimethylol derivative by substitution with two methylol groups in the ortho positions in relation to the hydroxyl group of the said substituted phenol, and the said dimethylol derivative is reacted with phenol to give a polyhydroxy phenol (I).

In the following description:—
 by "para-substituted phenol" there is meant phenol substituted in the para position in relation to the phenolic hydroxy group with an alkyl group having from 1 to 10 carbon atoms;

by "dimethylol derivative", or else by "dimethylol intermediate" there is meant the para-substituted phenol substituted with two methylol groups in the ortho positions in relation to the hydroxyl group;

by "polyhydroxy phenol" there is meant a compound according to formula (I).

The method for preparing the polyhydroxy phenol of this invention comprises the following stages:

(a) reacting formaldehyde and a substituted phenol of the formula:



where R is an alkyl radical containing from 1 to 10 carbon atoms, in a formaldehyde/phenol molar ratio of at least 2:1, in the presence of an inorganic base and at a temperature of at least 40°C, thereby to form a dimethylol derivative of said phenol;

(b) adding an acid to the reaction products of (a) in an amount at least equivalent to that of said inorganic base and in the presence of water, and separating the aqueous phase and the dimethylol derivative phase thus obtained;

(c) adding to said dimethylol derivative phase an organic solvent capable of dissolving said derivative, normally immiscible or slightly miscible with water and forming with the latter an azeotropic mixture, contacting the resulting solution with phenol in a molar ratio between said phenol and said derivative of at least 2:1, in the presence of an acid catalyst and at a temperature of at least 100°C, and maintaining the resulting mixture at boiling point until substantially complete reaction of said derivative with said phenol, while distilling the forming water as an azeotrope with said organic solvent; and

(d) recovering the polyhydroxy phenol from the reaction products of (c).

Stage a

According to the process of this invention formaldehyde is reacted with a para-substituted phenol, the latter being preferably chosen from para-tert-butylphenol, para-cresol, para-octylphenol, para-amylphenol and para-nonylphenol. The formaldehyde can be fed into the reaction medium as an aqueous solution, especially in the form of those commercial aqueous solutions which

- have a formaldehyde content of the order of 37—38% by weight. Low polymers of formaldehyde, such as paraformaldehyde, or anyway, any substance which frees formaldehyde under the reaction conditions can also be used for the purpose.
- The reaction is catalyzed by an inorganic base and preferably an alkali metal hydroxide, such as sodium, potassium or lithium hydroxide.
- The molar ratio of the formaldehyde to the para - substituted phenol is generally from 2:1 to 3:1 and that of the inorganic base to the said para - substituted phenol generally from 0.3:1 to 1:1.
- Further, the reaction is preferably carried out at a temperature of from 40° to 80°C and for a time such as to ensure complete reaction of the para - substituted phenol or at least until the concentration of the latter is reduced to values below 0.5% by weight in the reaction medium. The reaction time is generally from 1 to 4 hours.
- The way of contacting the reagents is not critical, but it is preferable to gradually add an aqueous solution of the inorganic base to the reaction medium containing formaldehyde and the para - substituted phenol, and to maintain the reaction mixture at the reaction temperature for a certain length of time at the end of the addition of the inorganic base.
- The reaction is generally carried out in the presence of water. Preferably, the reaction mixture should not contain more than 50% by weight of water.
- In the preferred embodiment, the molar ratio of alkali metal hydroxide to para - substituted phenol is maintained at about 0.5:1 and that of formaldehyde to para - substituted phenol at about 2.5:1. Further the reaction is carried out at a temperature of the order of 60°C, aqueous sodium hydroxide being fed gradually into the reaction medium. Under these conditions, the para - substituted phenol reacts almost completely with the formaldehyde in a period of about 2.5 hours.
- Stage b**
- An acid is added to the reaction products from stage a) in an amount at least equivalent to that of the inorganic base fed in stage a).
- Organic acids may be used for the purpose, but mineral acids, such as, for example, hydrochloric, sulphuric or phosphoric acids are preferable. Among the latter, phosphoric acid is preferred, for reasons of corrosion.
- The amount of acid which is generally added is that required to bring the pH of the medium to a value of from 6.5 to 2.
- Following the treatment with acid, the dimethylol intermediate becomes insoluble in water and it becomes possible to separate it from the aqueous phase containing the unreacted formaldehyde and the neutralization products of the inorganic base. Obviously, if stage (a) is carried out in the absence of added water, water is added in stage (b) of the process.
- In a preferred embodiment the reaction products from the first stage are cooled down to about 50°C and phosphoric acid is added gradually up to an equivalent ratio of sodium hydroxide to phosphoric acid of the order of 0.5:1. The mixture is then decanted at 40—50°C with separation of the aqueous layer (which is discharged) from the organic layer consisting essentially of the dimethylol intermediate.
- Stage c**
- To the dimethylol intermediate recovered in stage b) there is added an organic solvent capable of dissolving the said intermediate, normally immiscible or only slightly miscible with water and forming an azeotropic mixture with the latter.
- Particularly useful for this purpose are aromatic hydrocarbons such as toluene, xylene, cumene or other alkyl benzenes, boiling at a temperature not exceeding 160°C.
- To the solution thus obtained phenol is generally added in such amount as to ensure a molar ratio of the para - substituted phenol (fed in stage a) to the phenol, of from 1:2 to 1:3.5.
- The reaction is carried out at boiling point, generally at a temperature of from 100° to 160°C, the water which forms being distilled continuously in the form of an azeotrope with the preselected organic solvent.
- The reaction of the dimethylol intermediate with phenol is carried out in the presence of an acid catalyst, preferably an organic acid.
- The said acid should preferably have an acid dissociation constant, or else (in the case of a polybasic acid) a first acid dissociation constant which is greater than 1.10^{-5} . Examples of organic acids suitable for the purpose are: oxalic acid, benzoic acid, para - tert - butylbenzoic acid, salicylic acid and isophthalic acid.
- The amount of acid catalyst is generally from 0.1 to 5 parts by weight for every 100 parts by weight of phenol.
- Reaction times are those necessary for practically complete reaction of the dimethylol derivative and are generally from 2 to 4 hours.
- In a preferred embodiment, the solution of the dimethylol intermediate in the preselected solvent is added to the phenol and the catalyst, the reaction mixture being maintained at boiling point. The vapours which are evolved are condensed, with separation of an aqueous phase which is discharged, and of an organic phase, which is recycled into the reaction medium.

Stage d

The acid catalyst, the organic solvent, and any excess phenol are removed from the reaction products derived from stage (c).

5 In the case of the use of oxalic acid, the said acid is insoluble in the reaction medium at temperatures of the order of 30°—40°C. It can therefore be precipitated by cooling the reaction mass and can then be filtered.

10 In other cases it may be necessary to neutralize the acid catalyst and filter the precipitated salt.

15 The organic solvent and the excess phenol may be removed, the former by means of distillation at atmospheric or near atmospheric pressure, the second at a pressure lower than atmospheric, preferably by means of the thin film method. Obviously the said organic solvent and phenol can be re-used in the process for preparation of the polyhydroxy phenol. This latter remains in every case as a distillation residue.

20 By the process described the polyhydroxy phenol is obtained in its isomeric forms, which can be used as such for the purposes for which the polyhydroxy phenols are normally employed. Obviously, if wished, the various isomers can be separated by means of the usual methods, such as, for example, fractional crystallization.

25 The polyhydroxy phenols of this invention are especially useful as antioxidants for elastomers and plastics materials, as polymerization inhibitors for unsaturated monomers such as styrene and the alkyl esters of acrylic or methacrylic acid and as stabilizers for unsaturated polyester resins (products of the polycondensation of unsaturated polybasic acids and polyhydroxy alcohols, dissolved in styrene or another unsaturated monomer).

30 The polyhydroxy phenols of the invention are also useful for preparing epoxy resins by reaction with epichlorohydrin in an alkaline medium and the said epoxy resins are particularly suitable for paints with improved thermal and dimensional resistance, and resistance to chemical reagents.

35 Novolak phenolic resins with higher molecular weight than the conventional ones can be prepared by reacting the polyhydroxy phenols (I) in an acid medium with formaldehyde, possibly in the presence of phenol or phenolic compounds in general.

40 Resol phenolic resins can also be prepared in basic medium by reacting the same reagents in different ratios.

45 The said Novolaks are particularly useful when employed in combination with hexamine, as binders for mineral charges (for example sand for moulds or abrasives) or vegetable fillings, such as wood flour, or else as reinforcing or adhesives for rubber.

50 The said resols are particularly useful for impregnating paper and fabrics, for making laminates, or else, suitably modified with

vegetable oils, they can be used for hard and chemically resistant glossy stove enamels.

In the following experimental Example the parts and percentages are by weight unless otherwise specified.

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Example

Into a reactor furnished with an agitator, a steam heating system, a hypsometer, a reservoir for feeding in the reagents, a condenser, a demixer, a reflux duct for the condensate and collecting chamber for the distillate, there are fed in 426.7 parts of para - tert - butylphenol and 604 parts of a 36% aqueous solution of formaldehyde. The molar ratio of formaldehyde to para - tert - butylphenol is thus equal to 2.5:1.

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The temperature is taken to 60°C and 190 parts of a 30% aqueous solution of sodium hydroxide are added gradually to the agitated mass.

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At the end of the addition of the latter the molar ratio of para - tert - butylphenol to sodium hydroxide is equal to 2:1. After this addition the temperature is maintained at 60°C until the amount of free formaldehyde in the reaction medium is reduced to 4—4.5%.

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119 parts of a 75% aqueous solution of phosphoric acid are then added. Agitation is maintained until neutralization is complete. The agitator is then stopped and an aqueous phase containing unreacted formaldehyde and sodium phosphates, and an organic phase containing the dimethylol derivative of p - tert - butylphenol are separated.

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The aqueous phase is discharged, and 360 parts of toluene are added to the organic phase (720 parts), thus obtaining a toluene solution which has the following characteristics:

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dry matter	52%
viscosity at 25°C in cps	25
free para - tert - butylphenol	absent

This last determination was carried out by means of gas-chromatographic analysis.

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A mixture of 737 parts of phenol and 32 parts of oxalic acid, is heated to 100°C and the toluene solution of the dimethylol intermediate is added gradually to the heated mixture over a period of three hours. During this period of time the mass is kept boiling and the water is azeotropically distilled and is continuously removed through a demixer.

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The distilled toluene is recycled into the reaction medium.

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The temperature of the mass rises rapidly to 120—125°C during the addition of the toluene solution and remains at these values until the end of the said addition, the molar ratio of the phenol to the para - tert - butylphenol (fed in initially) in the reaction medium being then of 2.7:1.

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After the addition of the toluene solution the said temperature is maintained for 30 minutes and the mass is then cooled to 30—40°C.

- 5 At this temperature the oxalic acid, dispersed in the solution, is removed by filtering. The resulting solution has the following characteristics:

10	dry matter	64%
	viscosity at 40°C in cps	900
	free phenol	16%

This latter determination was carried out by means of gas-chromatography.

- 15 The solution is subjected to distillation at atmospheric pressure and 253 parts of toluene containing small amounts of phenol are distilled off.

- 20 The residue is distilled by the thin film method at a pressure of 3 mm Hg to remove the residual toluene and the unreacted phenol.

At the base of the evaporator about 1000 parts by weight of a polyhydroxy phenol having the following characteristics are recovered:—

25	appearance	solid
	melting point (in capillary)	74°C
	viscosity at 25°C in 50% ethanol solution	33 cps
30	pH in 50% ethanol solution	4
	Gardner melting colour	6
	free phenol (gas-chromatography)	<0.5%
	free para - tert - butylphenol (gas-chromatography)	absent

- 35 The product is soluble in most of the organic solvents.

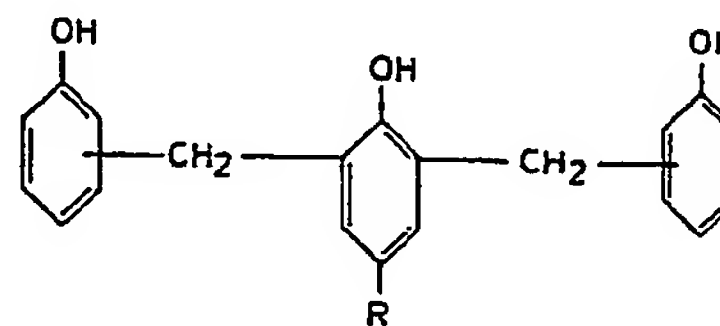
Analysis of the NMR spectra gives the following results:—

	$\bar{M}_n(OM)$ =average numerical molecular weight	364
40	\bar{n} =average number of hydroxyl groups per molecule	3.0
	R_A =average number of aromatic protons per ring	3.0
45	R_{MB} =average number of methylene bridges per benzene ring	0.6
	isomers ortho - ortho'	5%
	ortho - para	95%
	para - tert - butylphenol/phenol molar ratio	1:2

- 50 The product is therefore the polyhydroxy phenol of formula (I) in its two isomeric forms.

WHAT WE CLAIM IS:—

- 55 1. A polyhydroxy phenol defined by the formula:



where R is an alkyl radical containing from 1 to 10 carbon atoms, the methylene bridges being bonded to the central phenol ring in the ortho-positions in relation to the hydroxyl group, and to the other phenol rings in the ortho- or para-position in relation to the hydroxyl group.

2. A process for preparing a polyhydroxy phenol according to claim 1, characterized by:

(a) reacting formaldehyde and a substituted phenol of the formula:



where R is an alkyl radical containing from 1 to 10 carbon atoms, in a formaldehyde/phenol molar ratio of at least 2:1, in the presence of an inorganic base and at a temperature of at least 40°C, thereby to form a dimethylol derivative of said phenol;

(b) adding an acid to the reaction products of (a) in an amount at least equivalent to that of said inorganic base and in the presence of water, and separating the aqueous phase and the dimethylol derivative phase thus obtained;

(c) adding to said dimethylol derivative phase an organic solvent capable of dissolving said derivative, normally immiscible or slightly miscible with water and forming with the latter an azeotropic mixture, contacting the resulting solution with phenol in a molar ratio between said phenol and said derivative of at least 2:1, in the presence of an acid catalyst and at a temperature of at least 100°C, and maintaining the resulting mixture at boiling point until substantially complete reaction of said derivative with said phenol, while distilling the forming water as an azeotrope with said organic solvent; and

(d) recovering the polyhydroxy phenol from the reaction products of (c).

3. A process according to claim 2, characterized in that said substituted phenol is chosen from para - tert - butylphenol, para - cresol, para - octylphenol, para - amyl - phenol and para - nonylphenol.

4. A process according to claim 2 or 3, characterized in that said formaldehyde is fed into the reaction medium of (a) in the form of an aqueous solution or a substance which frees formaldehyde under the reaction conditions.

5. A process according to any one of claims 2 to 4, characterized in that said form-

aldehyde/phenol molar ratio is from 2:1 to 3:1.

6. A process according to any one of claims 2 to 5, characterized in that said inorganic base is an alkali metal hydroxide, the molar ratio between said inorganic base and said substituted phenol being from 0.3:1 to 1:1.

7. A process according to any one of claims 2 to 6, characterized in that stage (a) is carried out at a temperature of from 40 to 80°C.

8. A process according to any one of claims 2 to 7, characterized in that stage (a) is carried out for a period of from 1 to 4 hours.

9. A process according to any one of claims 2 to 8, characterized in that the reaction mixture of (a) does not contain more than 50% by weight of water.

10. A process according to any one of claims 2 to 9, characterized in that said acid of (b) is an inorganic acid.

11. A process according to any one of claims 2 to 10, characterized in that said acid of (b) is chosen from hydrochloric, sulphuric and phosphoric acids.

12. A process according to any one of claims 2 to 11, characterized in that said acid of (b) is added in an amount such as to bring the pH to a value of from 6.5 to 2.

13. A process according to any one of claims 2 to 12, characterized in that said organic solvent is chosen from among the aromatic hydrocarbons having a boiling point not exceeding 160°C.

14. A process according to any one of claims 2 to 13, characterized in that said phenol of (c) is used in an amount of from 2 to 3.5 moles for each mole of substituted phenol used in (a).

15. A process according to any one of claims 2 to 14, characterized in that said mixture of (c) is boiled at a temperature of from 100 to 160°C.

16. A process according to any one of claims 2 to 15, characterized in that said acid catalyst is an organic acid.

17. A process according to any one of claims 2 to 16, characterized in that said acid catalyst is an acid having an acid dissociation constant, or else (in the case of a polybasic acid) a first acid dissociation constant above 1.10^{-5} .

18. A process according to any one of claims 2 to 17, characterized in that said acid catalyst is chosen from oxalic, benzoic, para - tert - butylbenzoic, salicylic and isophthalic acids.

19. A process according to any one of claims 2 to 18, characterized in that said acid catalyst is used in an amount of from 0.1 to 5 parts by weight for each 100 parts of phenol.

20. A process according to any one of claims 2 to 19, characterized in that stage (c) is carried out for a period of from 2 to 4 hours.

21. A process according to any one of claims 2 to 20, characterized in that said polyhydroxy phenol is recovered by precipitating the acid catalyst and removing the resulting precipitate, and distilling off the organic solvent and the unreacted phenol present in said reaction products of (c).

22. A process according to claim 2, substantially as hereinbefore described with reference to the Example.

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